36p.

N64-15189
CODE-1
CR-55647

[redacted]

OTS PRICE

XEROX $ 3.60 ph.
MICROFILM $ 1.28 mf.

Alkaline Battery Division

GULTON INDUSTRIES, INC.

Metuchen, N. J.

t: DESIGN, DEVELOPMENT AND MANUFACTURE

OF STORAGE BATTERIES FOR FUTURE

SATELLITES VII / Quarterly... No. 7, 4 May

— 4 Aug. 1962

Report No. 7

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION - NASA CONTRACT NO. NAS 5-809

(NASA CR-55647) OTS:

SEVENTH QUARTERLY PROGRESS REPORT

4 May 1962 to 4 Aug. 1962

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J. Liska 1962 36p

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Alkaline Battery Division

Metuchen, New Jersey

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I. ABSTRACT

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Improvements in the pilot plant facility have progressed along the lines of introducing recording equipment to continuously monitor cell voltages and current, and fabricating setups to automate and simplify the handling of batches of cells as they go through electrical processing.

Deep drawn containers for VO-6HS cells have been fabricated and the problems and wrinkles have been ironed out. Cells using these new containers are in process.

Hardware for the VO-50HS cell is being fabricated. Electrode stacks are being formed. Cells will be assembled within 30 days and electrically tested.

Thin plate experimental VO-5X cells were fabricated, checked out electrically and compared to a standard VO-6HS cell.

Six VO-6HS lab cells were cycled in a 70% depth, 3-hour routine for 560 cycles, and performed well. The cycle was then reduced to 90 minutes, and 800 cycles have been reached, again with 70% depth. One cell failed by shorting across the separator.

Some studies have been made on the capacity spread of VO-6HS cells and the charge efficiency of these cells is discussed. Reference electrode measurements were made to determine which electrode limits capacity.

Author

II. PILOT FACILITY

The pilot facility to produce hermetically sealed cells for aerospace applications is essentially complete. Most of the fo equipment necessary to produce satisfactory sealed cells has been installed and is functioning. Since the facility is small, and complete inspection at many points along the line is mandatory, the output per month is small. During the past quarter efforts have been directed at increasing output through automation, reducing the number of rejects, and collecting data automatically during processing.

Once cells are fabricated, they are then subjected to a careful electrical and mechanical checkout, designed to eliminate all leaks, shorts, high pressures or low capacities. Cells have been manually handled in groups of 25, with an operator making all operations and recording all data. Several multipoint recorders have been procured to monitor cell voltages and current continuously.

In addition, a "cell conditioning control rack" has been designed, and is partially fabricated, to facilitate handling during this operation. The purpose of this equipment is to eliminate unnecessary handling of cells during the electrical processing phase of manufacturing the hermetically sealed cells. Normal processing procedure requires each individual cell to be connected and removed from the circuit three times to be pumped down, or for gases to be admitted such as the helium tracer before closure. This is very time consuming, and allows possible damage to the cell due to handling. The control rack was mechanically designed, keeping in mind the need to conserve time and decrease handling. Each cell is connected into a manifold section using a stainless steel quick-disconnect. A stainless steel toggle valve is also included in each line to seal off the cell during processing, but to allow quick access to the manifold. The manifold is provided with helium, oxygen, or vacuum exhausting. A schematic of the system for 3 cells is shown in Figure 1.

Also shown in Figure 1 is the schematic of the electrical hookup for the cells. As processed now, during a capacity discharge, cells are removed one at a time as they reach 1.0 volts per cell. Sometimes during a discharge of a batch of 25 cells some quite adept juggling of clip leads is necessary toward the end of charge. Hopefully, very uniform cells should all reach 1.0 volts at about the same time, and therefore, some provision is necessary for more facility of electrical operations. With the electrical hookup being provided in the new "cell conditioning control racks", each cell is wired into place. Connection to each cell terminal is by screw lugs rather than clip leads, and individual voltage sensing leads are provided. This eliminates probing with voltmeter picks. During discharge, a cell may be shunted by a switch operation when it approaches zero volts. Thus the discharge circuit will never be momentarily broken, ensuring a better measure of discharge ampere hours.

The monitoring of cell voltage is accomplished by the use of a rotary switch and a voltmeter. Current is controlled by a variable resistor and an ammeter tied into the control rack. All these refinements are incorporated on a master panel which is mounted directly in front of the cells being processed.

III. DEEP DRAWN CELL CONTAINERS

The development of deep drawn cell containers came about with the need to improve hermetically sealed cells for space applications. Three major factors make the drawn can a superior container over the present weldment. First, the drawn container dimensionally can be made to closer tolerances. Second, the strength of a drawn unit is approximately three (3) times greater than that of a welded unit of the same material. Third, there are fewer seams that might normally allow the possibility of leakage. Aside from the above mentioned improvements, the question of weld slag contaminating the cell always arises. Deep drawn cans minimize this since only one weld occurs - the final weld of the header to the can.

To meet existing dimensional requirements, the deep drawn container had to be similar to the welded can used. This required special tooling not normally found in establishments doing this type of work. The corners and radius had to be held to close tolerances as well as the depth of draw. To accomplish this, eight (8) separate developments had to be made. This proved to be a trial and error operation, to flow the material to the proper location for the next draw. After each drawing operation the material must be annealed because it work hardens during the preceeding operations.

The final finish of the surface of the cans caused more of a problem than anticipated. The sides and faces had to be smooth and free from any disfigurations. To accomplish this, the side had to be ironed first and then annealed. Then the faces had to be ironed. The annealing, after ironing the faces, was eliminated to retain added stiffness in that portion of the can which would normally tend to bulge with any internal pressure.

The present batch of containers have been through the eighth and final draw, and show promise of being the type of container that is desired for space use. Figure 2 is a photograph of the drawn can VO-6HS and the welded can cell.

IV. 50 A.H. HERMETICALLY SEALED CELL

Design-wise, the 50 AH hermetically sealed cell differs in many ways from previous designs. Normally, the hermetic seal was formed by making a ceramic-to-metal seal between the cover and the ceramic insulator, in addition to between the terminal and ceramic insulator. In the present design, neither of the two terminal posts forms part of the hermetic seal. This allows freedom in the choice of materials from which the terminal can be made. The material that has been chosen is copper, which allows good heat transfer and has better electrical conductivity.

For the hermetic seal at the positive terminal, the upper end of the ceramic insulator has a seal ring attached by a ceramic-to-metal bond. At the lower end, the lower seal ring is also attached by a ceramic-to-metal bond. Both these seals are compression seals. The copper terminal, which passes through the center of the insulator is silver soldered to the terminal base. The upper face of the terminal base is heliarc welded to the bottom face of the lower seal ring completing the hermetic seal. At the lower end of the terminal base is a plate which is slotted parallel to the direction of the electrodes. The tabs of the nickel electrodes are notched so that they can be slipped into the slots and welded, thereby allowing a reduction in case height compared to the usual method of using combs.

The negative terminal is grounded to the case so that the copper terminal is silver soldered to the cover. The electrodes are welded into the comb and the comb is attached to the cover by a comb support. The cover is made by drawing, and the case is fabricated.

Most of the case and terminal components necessary for the production of the 50 AH hermetically sealed cell have been ordered and are being fabricated by outside suppliers. The electrodes have been fabricated and the electrode stacks have been assembled. At the present time, the electrodes are undergoing formation in tanks by the usual pilot plant procedure. Figure 3 shows the 50 AH cell stack as compared to a VO-6HS cell stack. Figure 4 shows the electrode stacks for the 50 AH cell undergoing tank formation.

V. THIN PLATE CELLS

As indicated in the last quarterly report, the hardware for thin plate cells was fabricated and after some preliminary studies on prototypes, five cells were assembled to operate as sealed cells. The electrodes are 0.025 to 0.027 inch thick as compared to the standard 0.035 inch plate. Because the porosity of the thin plate electrodes was 25% greater than that of the thicker plates, it was found that separate tank formation of the electrodes was not necessary. Therefore, after assembly the five cells were filled with 13.5 ml of electrolyte, evacuated, and sealed. The cells were charged at 0.5 amperes and then put on overcharge at the same rate. At the steady state, the voltages and pressures were recorded while the cells were maintained at 25 $\pm 0.5^{\circ}$C in an oil bath. The overcharge current was increased to 0.75 amperes until the steady state was again reached. Then the overcharge current was increased to 1.0 ampere and maintained until the steady state was obtained. The observed pressure versus overcharge current is shown in Figure 5. The overcharge current is expressed as a fraction of the cell capacity. The slope of the line representing the average of the five thin plate cells is given as 40 ma/psi.

In addition, Figure 5 also gives the observed pressure versus the overcharge current for typical VO-6HS and VO-20HS nickel-cadmium cells. As shown, not only is the slope less for the VO-5X cell, but the overall pressures are lower. One reason for this phenomena is believed to be that the surface area of the electrode per ampere hour is greater in the thin plate cells than the others.

Figure 6 illustrates the cell voltage as a function of the overcharge current. The overcharge current is expressed as a fraction of cell capacity. In addition, the curves for a typical VO-6HS and VO-20HS nickel-cadmium cell are given for comparison. The voltages appear to indicate that the thin plate cells are operating at a lower current density which is consistent with the previous hypothesis regarding pressures, i.e. that the surface area of the thin plate electrodes per ampere hour is greater.

After the overcharge, the cells were discharged at the C/2 rate. The capacity to 1.0 volts was 5.75 AH. They were then recharged manually at 0.5 amperes and put on cycling which discharged the cells to a 40% depth and returned 120%. The discharge portion was 3.9 amperes for 35 minutes, 2.28 AH, while the charge portion was 3.0 amperes for 55 minutes, 2.74 AH. The cells were cycled 31 times. Table I gives the beginning of discharge, end of discharge, beginning of charge, and the end of charge voltages for cycle 1, cycle 14, and cycle 31.

TABLE I.

CELL VOLTAGES AS A FUNCTION OF CYCLE NUMBER

Cycle Number	Charge Voltages		Discharge Voltages	
	Beginning	End	Beginning	End
1	1.30	1.46	1.29	1.22
14	1.20	1.47	1.35	1.19
31	1.27	1.48	1.34	1.18

After the 31 cycles, the cells were placed on a 0.5 ampere continuous charge for 24 hours. A C/2 rate discharge was conducted and the capacity obtained was 4.62 AH. The cells were recharged at 0.5 amperes and then overcharged at 1.0 ampere.

A C rate, 5. A, discharge was conducted, and the capacity obtained was 4.74 AH to 1.0 volt. Figure 7 illustrates the performance. For comparison a C rate discharge for a typical VO-6HS cell is added to the same figure.

They were recharged at the C/10 rate and then overcharged to insure that the cells were in a fully charged state. After a 24 hour stand time, at 25°C, the open circuit voltage was measured and found to be 1.30 volts. Then a 2.0 ampere discharge was conducted for a few seconds. The discharge was immediately changed to a 4.0 amperes for a few seconds. In a similar manner the 6.0, 8.0, and 10.0 ampere discharges were conducted. The cell voltages were obtained immediately on initiation of a discharge. The results are given in Figure 8. The slope obtained is -0.008 while the slopes obtained from a VO-6HS cell when discharged immediately after charging is -0.006.

After a 0.5 ampere charge and overcharge a 2C, 10 amperes discharge was conducted. The capacity to 1.0 volt was 4.13 AH and is shown in Figure 9.

The cells were again charged and overcharged at 0.5 amperes. A 4C, 20 amperes discharge was performed, after a one hour stand time, giving a capacity to 1.0 volt of 2.82 AH as shown in Figure 9. To determine the cell capacity after the number of discharges already performed, the cells were charged and overcharged at 0.5 amperes. A C/2 rate discharge was conducted and the capacity, obtained to 1.0 volt was 5.0 AH. Figure 9 shows the discharge.

Using thin plate electrodes, it was found possible to place the cells into immediate service. The electrodes did not require a lengthy formation process which involves wrapping and rewrapping of the separator, in addition to washing and drying the electrodes.

Below is a table comparing some of the characteristics of the VO-5X, VO-6HS and VO-20HS nickel-cadmium cells.

TABLE II.

COMPARISON OF SEALED CELLS

	VO-5X	VO-6HS	VO-20HS
WEIGHT (Lbs.)	0.47	0.62	1.9
CELL DIMENSIONS (in)			
LENGTH	2.09	2.09	2.98
WIDTH	0.81	0.81	0.89
HEIGHT	2.91	3.67	6.58
VOLUME in^3	4.92	6.15	17.44
WATT-HOURS	5.63	8.28	23.5
WATT-HOURS/Lb,	12.0	13.4	12.4
WATT-HOURS/in^3	1.14	1.35	1.35

It may be concluded from these studies that no significant advantage in watt-hours per pound is achieved through the use of thinner plates. This is due to the fact that more thin plates are required, and as a result, more folds of separator are necessary.

The advantages of thinner plates are that they apparently have a larger surface area per ampere hour of electrode capacity. As a result, the discharge voltage at comparable rates is slightly higher than for thicker plate cells. In addition, overcharge voltages and pressures are lower at equivalent C-rates.

VI. ELECTRICAL PERFORMANCE OF VO-6HS CELLS

A. CYCLING

Six laboratory cells of the VO-6 type were fabricated and electrically checked out by charging them at 0.6 amps for 5 days, and discharging them to 1.00 volts at a 3.0 ampere rate. This was repeated and the capacities were determined. The average capacity was 6.67 ampere hours with a spread of 0.70 ampere hours.

The cells were fully charged and overcharged for two days at 0.6 amps (C/10) after which they were placed on a 70% depth of discharge cycle consisting of a 60 minute discharge at 4.2 amperes followed by a 120 minute charge at 2.4 amperes. This charge was found to be insufficient and was increased after a few cycles to 2.5 amps or a 19% overcharge.

These cells continued cycling for 560 cycles. A typical cycle curve from one of these cells at cycle #500 is shown in Figure 10. A three hour cycle had been selected because of a lack of cycling data on this size cell, but since they were responding normally to this cycle, it was decided to change the cycle to a 90 minute cycle. At the end of the 560th. cycle, the average end of charge voltage was 1.50 with a spread of 0.03 volts. The cells were taken off cycle at the end of charge and placed on 0.6 amps for two hours and then discharged at 3.0 amps (C/2). The average capacity was 4 ampere hours with a spread of 0.2 ampere hours. The cells were exhibiting the "memory effect" and at 70% depth were exhibiting just the capacity being cycled. Some cells were below 1.0 volts at the end of discharge. The cells were shorted after discharging to 0.60 volts and left shorted for 16 hours. They were recharged at 0.6 amps and 16 hours. They were recharged at 0.6 amps and left on overcharge for 5 days. The average overcharge voltage was 1.39 with a spread of 0.04 volts.

The cells were then put on a 90 minute cycle consisting of a 35 minute discharge at 7.2 amps and a 55 minute charge at 5.5 amps or a 20% overcharge.

After 800 cycles, it was noted that the end of discharge voltage of one of the cells was down to 0.50. Cycling was stopped at the end of charge after 800 cycles and the cells placed on a 0.6 amp overcharge.for 16 hours. The capacities were checked at a C/2 rate. Two cells had 6.2 ampere hours, two had 6.0 ampere hours, and one had 5.7 ampere hours, and one cell had 3.9 ampere hours. This cell was the same one that had an end of discharge voltage of 0.50 v volts. Upon returning the cells to a 0.6 ampere charge, this cell indicated a partial short. The cell was disassembled and a burned spot found in the edge of the separator between plates.

The remaining cells were recharged at 0.6 amps and overcharged for 5 days at the same rate. The capacities were again determined at 3.0 amp discharge rate, and the average capacity was 5.72 ampere hours with a spread of 1.0 ampere hours. The cells were recharged again and are to be put back on cycle.

As has been noted in other tests, continuous repetitive cycling does not result in irreversible loss of capacity. Even though the cycled cells assume a capacity about equal to the depth of the cycle routine, the full nominal capacity is recoverable after a C/10 overcharge. Separator failure (shorted cell) still appears to be the most likely cause of cell failure.

B. CAPACITY AND CHARGE EFFICIENCY

Several hundreds of VO-6HS cells have been produced in the pilot plant since it started to function, and one characteristic which persists to date is the non uniformity of cell capacities. A range of cell capacities from 5.5 to 8.0 ampere hours has been produced by what appears to be an identical fabricating procedure. In addition, the plates used in the cells are identical in capacity. At one time each individual electrode was discharged separately, but it was decided that this was time consuming and unnecessary. Therefore, electrode stacks are processed and an electrode stack must deliver 7 ampere hours for it to be usable in VO-6HS cells.

It has also been observed that successive discharges of the same VO-6HS cell will not always yield the same value of capacity. This observation led to the hypothesis that perhaps the non uniformity in capacity is due to the nature of the hermetically sealed nickel-cadmium cell. Another observation has been made, particularly with VO-20 size cells, that after continuous repetitive cycling, a group of cells operating in series, become more uniform and capacity slowly increases. Several further observations have shown that in some cases a 20 to 24 hour charge at 0.6 amperes will not result in 6 ampere hours on the following discharge at 3 amperes, while a high rate charge, say at a constant voltage of 1.45 volts per cell, will result in over 6 ampere hours. It is also observed that a continuous overcharge at 0.6 amperes for 72 hours (over a weekend) results in higher capacity than a 0.6 ampere charge for only 21 hours.

Table III shows the capacity of 6 cells which had been fabricated in the pilot plant and which originally had capacities between 5.40 and 5.90 ampere hours. Several different charge procedures were run to see their effect on the subsequent capacity discharge.

CELL NO.	1	2	14	ORIGINAL CAPACITY	
A	4.40	4.80	4.70	5.40	
B	5.15	5.55	5.85	5.55	
C	5.85	6.05	5.70	5.50	
D	4.55	5.00	5.40	5.60	
E	6.00	6.20	4.90	5.45	*shorted
F	5.70	5.70	5.80	5.90	
G	5.30	5.25	5.20	5.20	
H	6.05	6.00	5.75	6.15	
I	6.05	6.25	5.80	6.00	
J	6.10	6.15	5.95	6.40	
K	6.40	6.70	5.95	6.30	
L	5.25	5.25	5.50	5.45	

* Deep Drawn

After 10, 50% depth
repetitive cycles

3.0 amps for 2 Hrs.
0.75 amps for 48 Hrs.

Figure 2 shows a plot of capacity versus cycle number and indicates the charge routine to which the cell was subjected. Note that the higher rate charges from cycle 8 on were beneficial.

These observations suggest that in some VO-6 cells the charge efficiency at low rates for short times is poor.

Poor charge efficiency has always been attributed to the positive electrode which begins to gas O_2 at about the half charged point. Experiments were run on VO-6HS cells which were completely discharged, vented, and then discharged into reverse to see if either electrode was present in any excess. As manufactured, both electrodes are completely discharged at the time of assembly. Imbalances do occur during abnormal operation due to loss of gases through a faulty seal, and apparent imbalances can occur during high rate charges and discharges due to unequal polarizations of the electrodes.

It is interesting to note that if either electrode outlasts the other on discharge, a cell voltage of -0.1 volt is obtained so that cell voltage alone is insufficient to determine which electrode is limiting. This is borne out by an analysis of reference electrode measurements as discussed below.

Using a Hg/HgO reference electrode, the following reactions are obtained during discharge and reversal.

Electrode	Discharge	Reversal
Ni - Ref	+0.4 V	H_2 is formed at -1.0
Ref - Cd	-0.9 V	O_2 is formed at +0.5 V

$$E\ cell = E_{Ni} - E_{Cd}$$

If the positive electrode runs down first

$$E\ cell = -1.0 - (0.9) = -0.1\ V$$

If the negative electrode runs down first

$$E\ cell = +0.4 - (+.5) = -0.1\ V$$

Thus a second discharge plateau at -1.0 volt may be due to either positive or negative limiting capacity. A reference electrode measurement is necessary.

Figure 12 shows a plot of reference electrode potentials for a VO-6HS cell which was produced in the pilot plant. It showed a low capacity and was therefore punctured and discharged with a reference Hg/HgO electrode inserted. Note that the positive active electrode was 7.25 AH while the negative was only 5.9, causing low capacity for the cell.

VII. CONCLUSIONS

Steps have been taken to automate pilot plant operations and to collect processing data continuously and automatically.

The deep drawn can for VO-6HS cells is available.

Large size 50 AH cells are completely designed and are being fabricated from both in house fabricated parts and subcontracted parts.

No significant advantage in watt-hours per pound is achieved through the use of thinner plates. This is due to the fact that thin plates require more separator and result in a bulkier pack and more terminal hardware. The advantage of thinner plates are that they have a larger surface area per ampere hour of electrode capacity and as a result overcharge voltage and pressures are lower than for thicker plate cells at equivalent C-rates.

VO-6HS have been cycled over 1800 cycles at 77^{o}F at a 70% depth of discharge. The memory effect wherein the cells begin to exhibit the capacity to which they are being cycled has been observed. The full rated capacity is recoverable after a C/10 overcharge.

The capacity of VO-6HS cells is sensitive to the charge conditions for the previous charge. High rate charges give higher capacity; at 0.6 ampere the charge efficiency is apparently poor in some cases.

VIII. PROGRAM FOR THE NEXT PERIOD

The main items of effort for the next period will include:

1. Complete fabrication of the 50 AH hermetically sealed cell, and determine the electrical characteristics of the cell.

2. Some further electrical characteristics of the thin plate cells will be determined, and the cells will be cycled continuously to see if any deterioration occurs during cycle routine.

3. VO-6 HS cells in drawn cans will be fabricated and delivered.

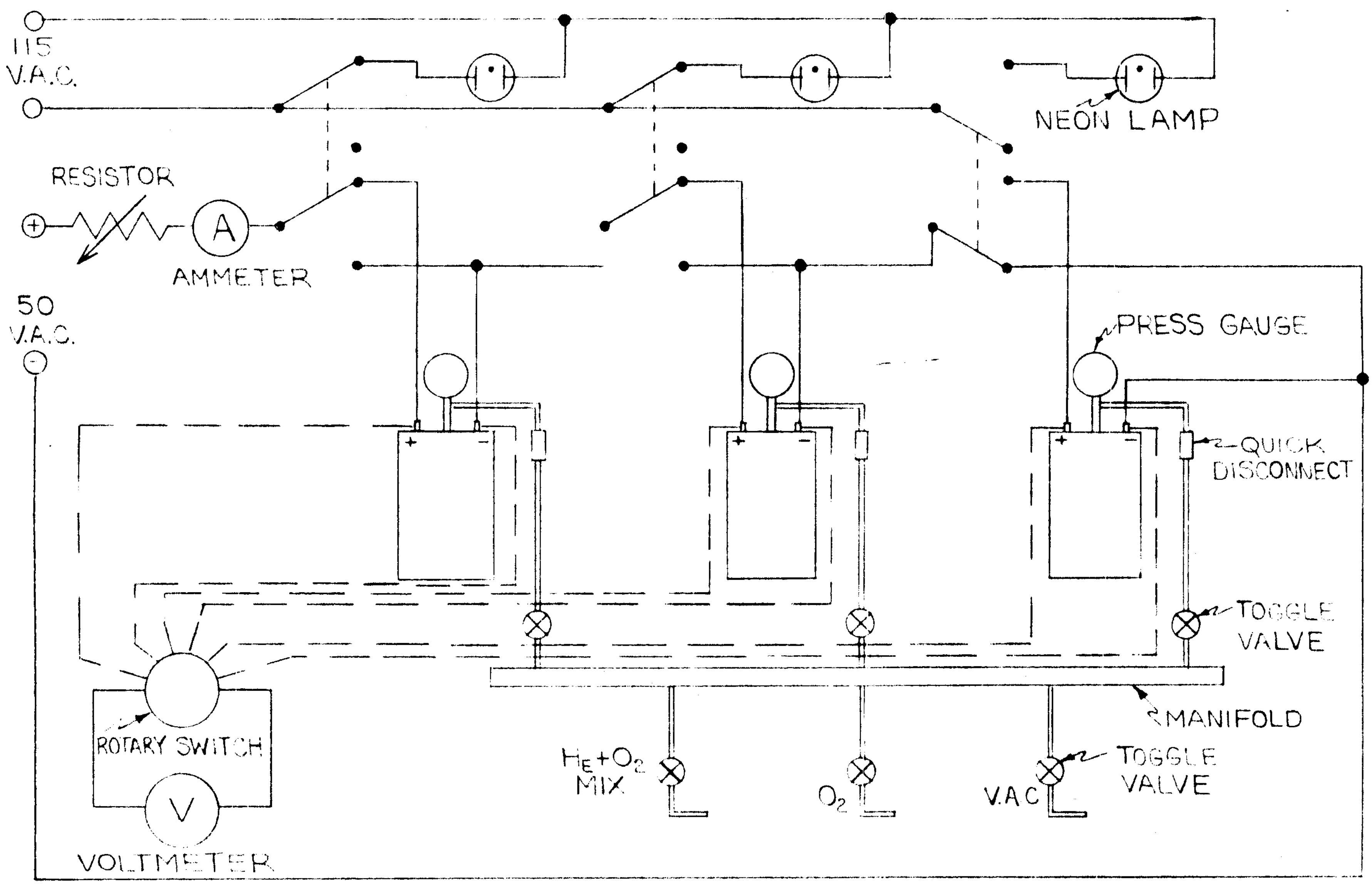
4. Consideration will also be given to charge efficiency and low temperature charge techniques.

IX. PERSONNEL

The following staff personnel have contributed to this effort.

R. C. SHAIR	DIRECTOR OF RESEARCH
G. RAMPEL	SENIOR CHEMIST
J. LISKA	CHEMICAL ENGINEER
R. DAGNALL	MECHANICAL ENGINEER

FIG. 1



SCHEMATIC of CELL CONDITIONING CONTROL RACK

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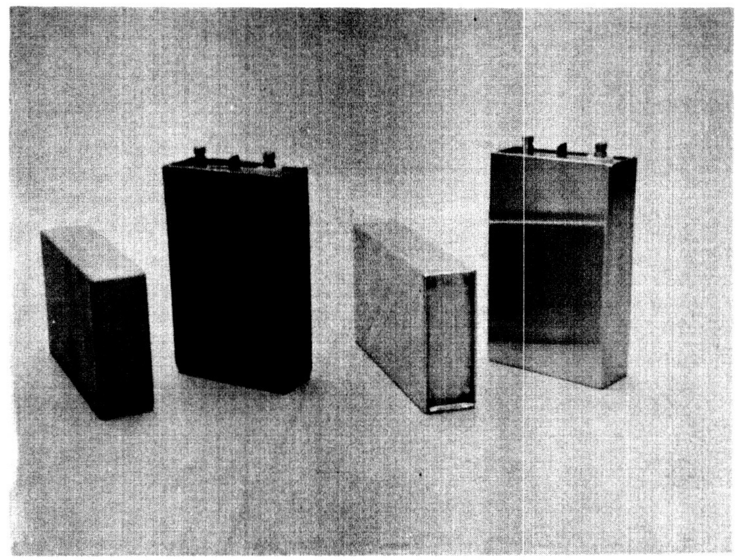

FIGURE 2
DRAWN AND WELDED CAN VO-6HS CELLS

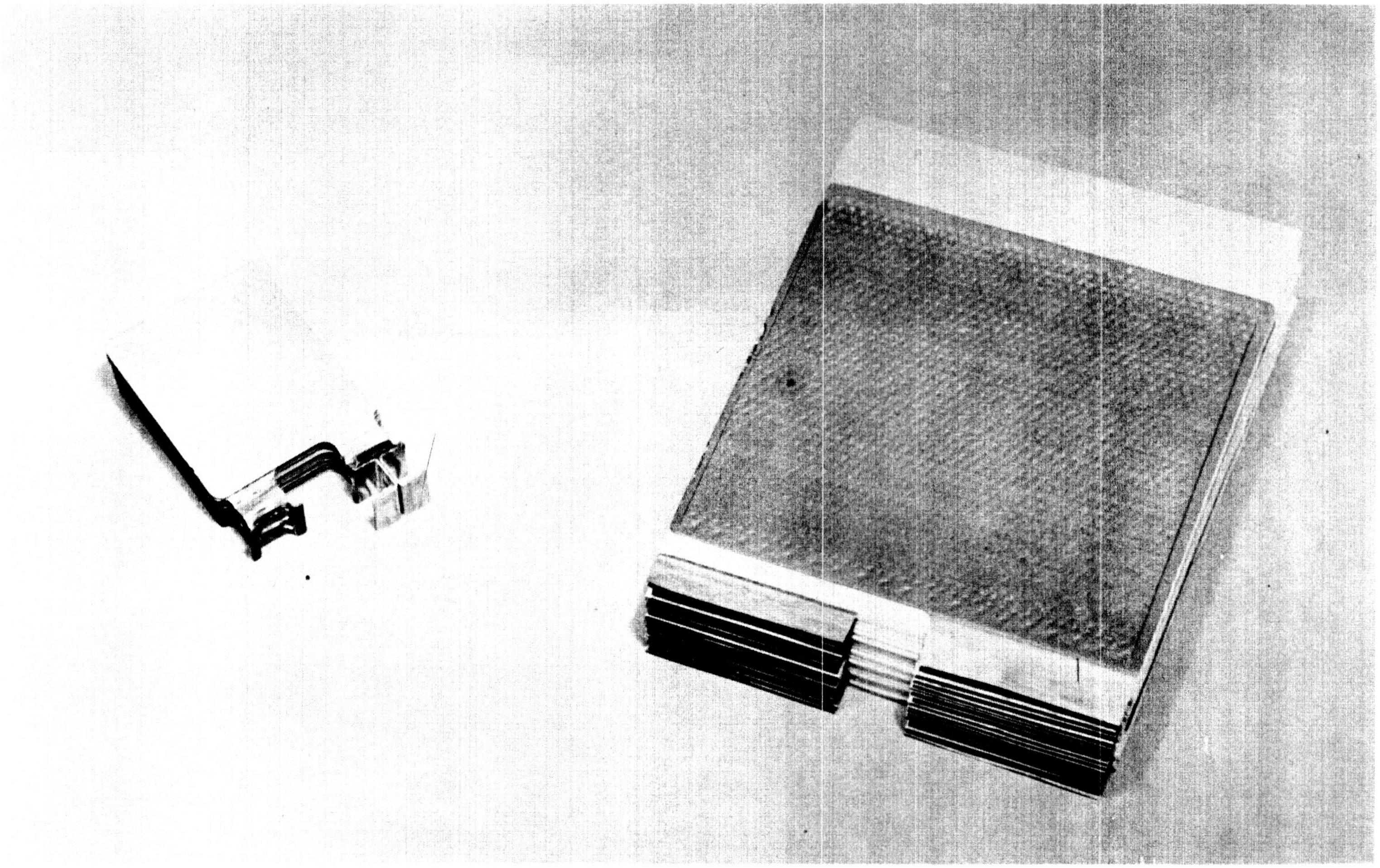

FIGURE 3
50 AH SEALED NICKEL-CADMIUM ELECTRODE ASSEMBLY
(6 AH ASSEMBLY AT LEFT FOR COMPARISON)

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Alkaline Battery Division
Metuchen, New Jersey

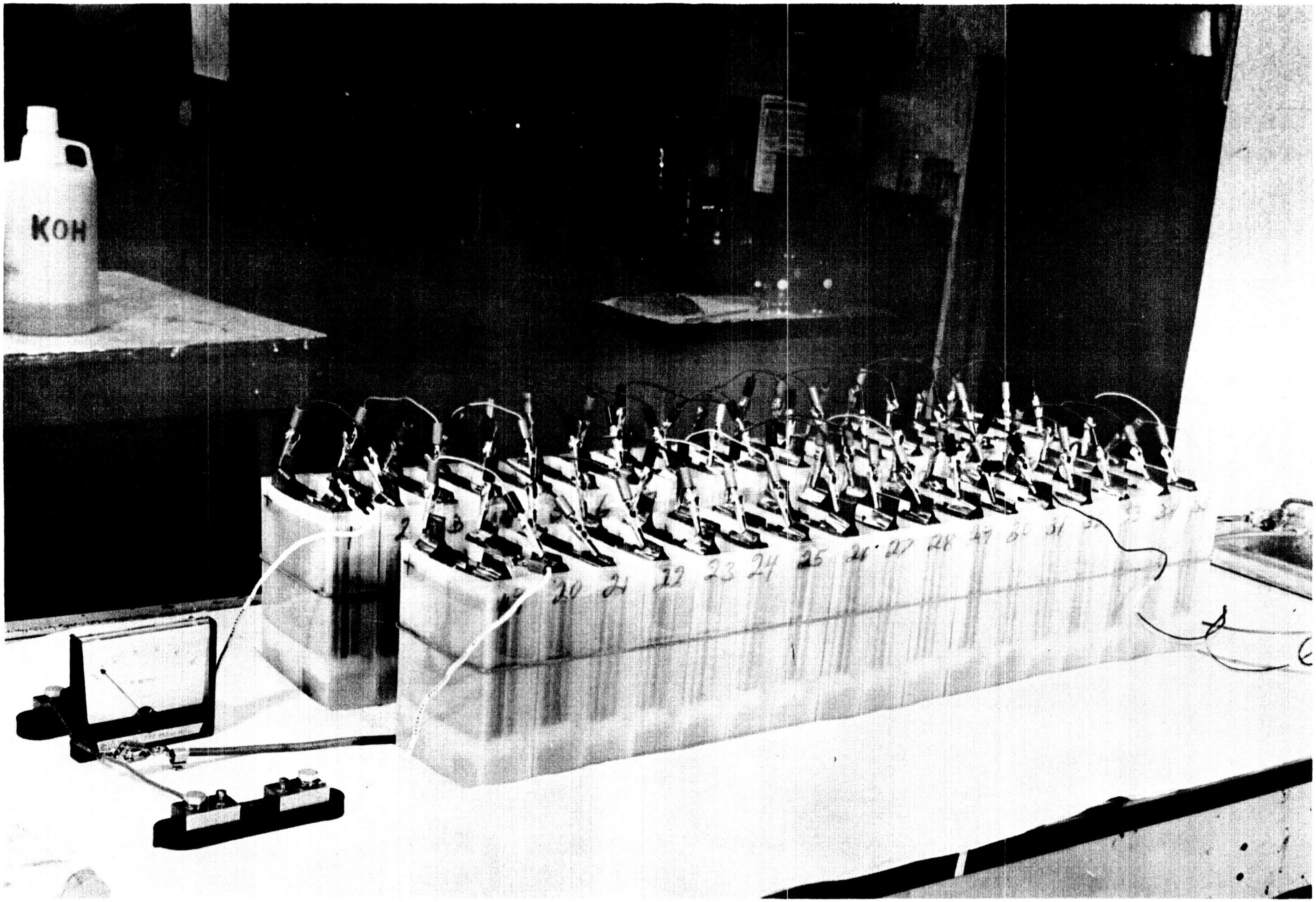

FIGURE 4
ELECTRODE STACK FORMATIONS FOR 50 AH CELLS

FIG. 5

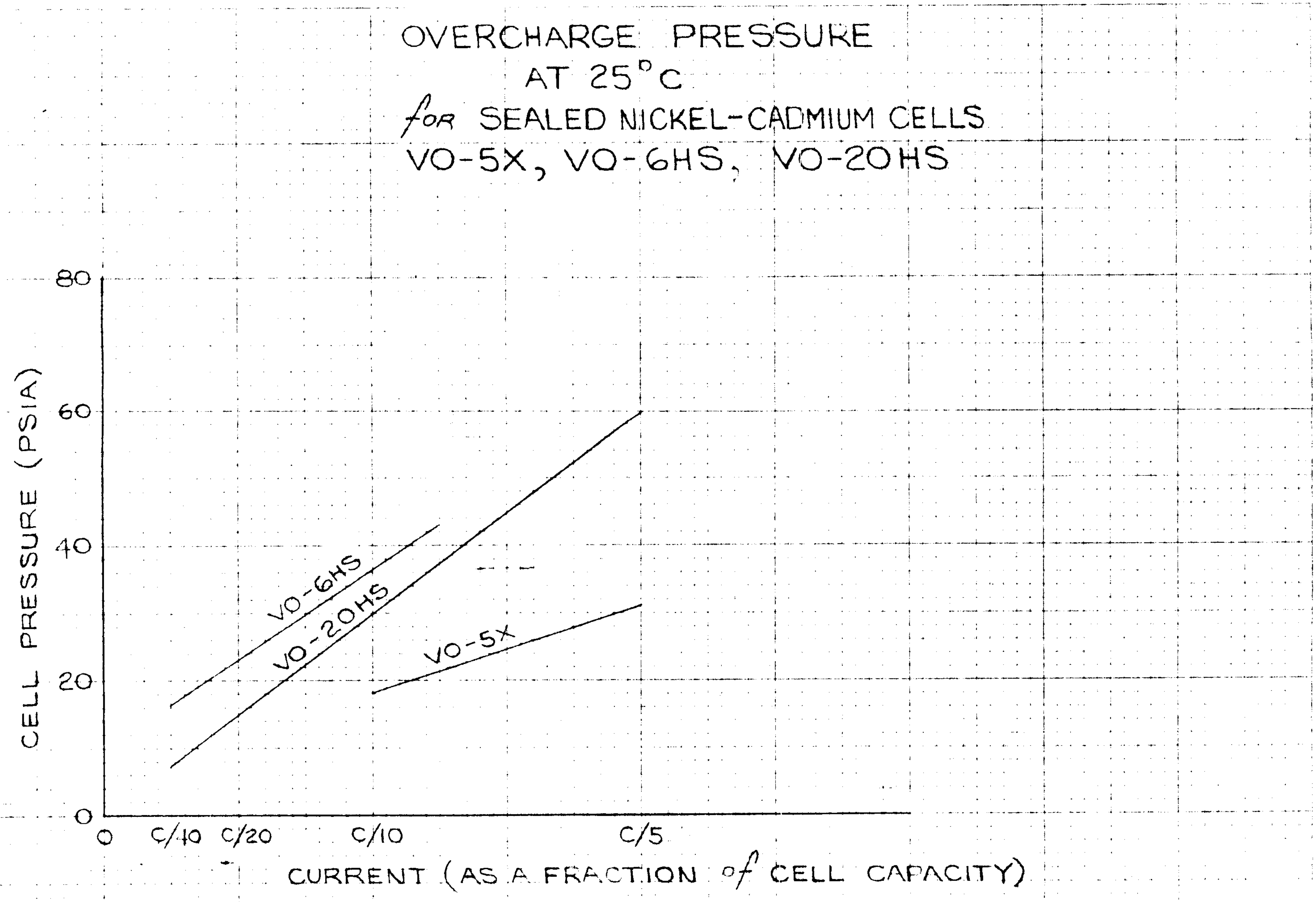

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FIG. 6

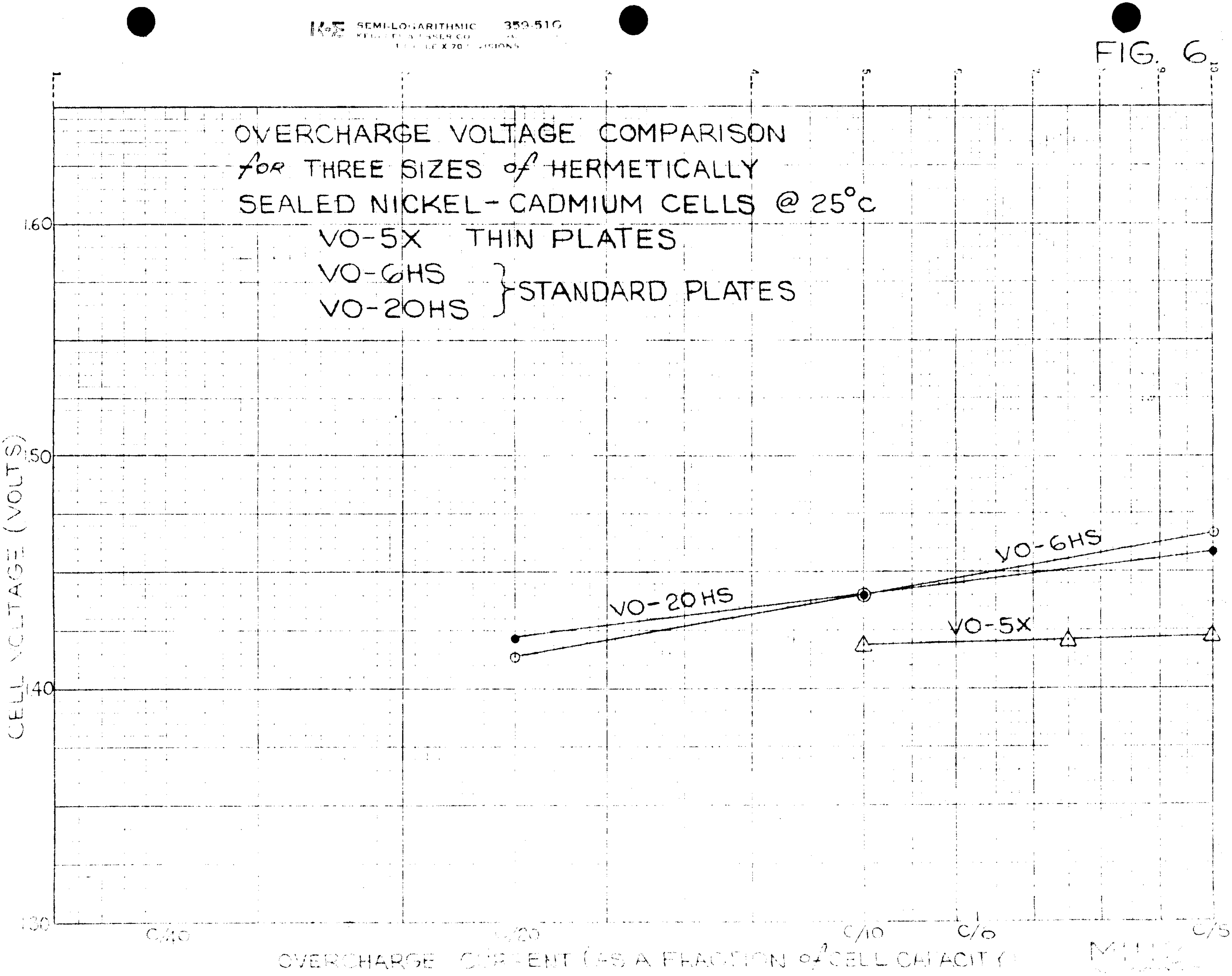
K+E SEMI-LOGARITHMIC 359-51G
OVERCHARGE VOLTAGE COMPARISON
for THREE SIZES of HERMETICALLY
SEALED NICKEL-CADMIUM CELLS @ 25°C
VO-5X THIN PLATES
VO-6HS
VO-20HS
STANDARD PLATES
VO-6HS
VO-20HS
VO-5X
1.60
1.50
1.40
1.30
CELL VOLTAGE (VOLTS)
C/40
C/20
C/10
C/6
C/5
OVERCHARGE CURRENT (AS A FRACTION of CELL CAPACITY)

FIG. 7

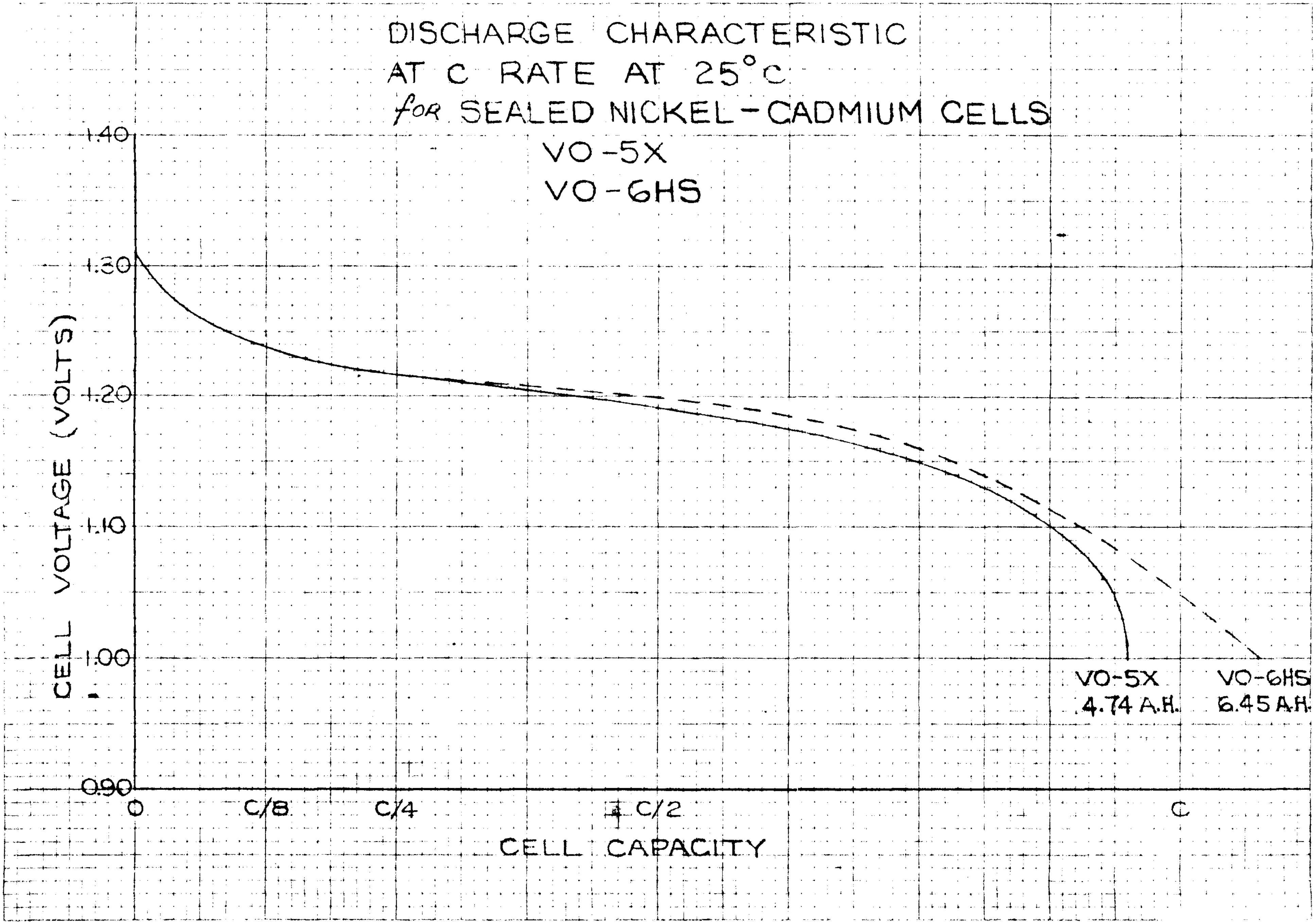

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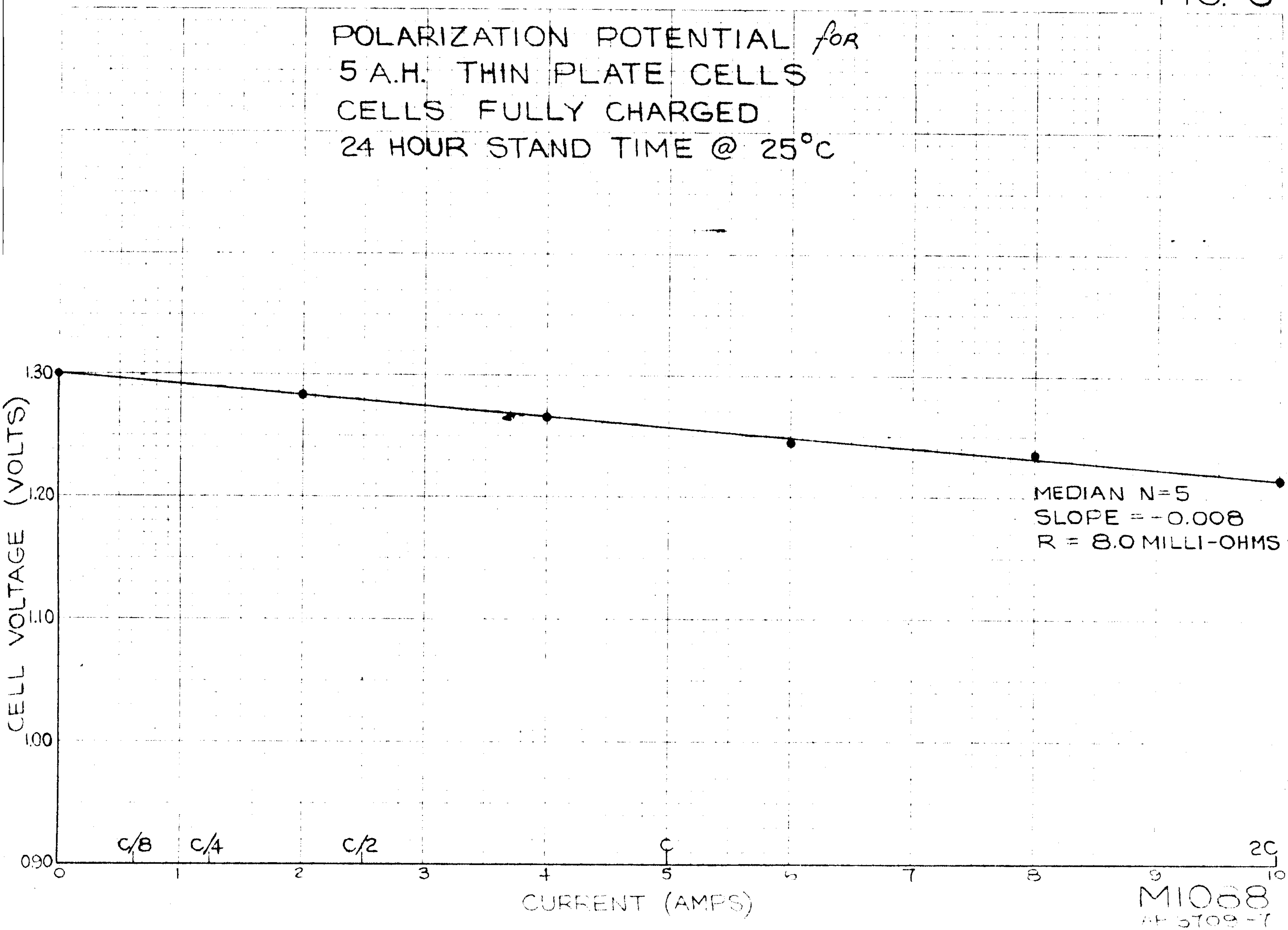
FIG. 8


POLARIZATION POTENTIAL for
5 A.H. THIN PLATE CELLS
CELLS FULLY CHARGED
24 HOUR STAND TIME @ 25°C
CELL VOLTAGE (VOLTS)
1.30
1.20
1.10
1.00
0.90
CURRENT (AMPS)
0
1
2
3
4
5
6
7
8
9
10
C/8
C/4
C/2
C
2C
MEDIAN N=5
SLOPE = -0.008
R = 8.0 MILLI-OHMS

M1068

FIG. 9

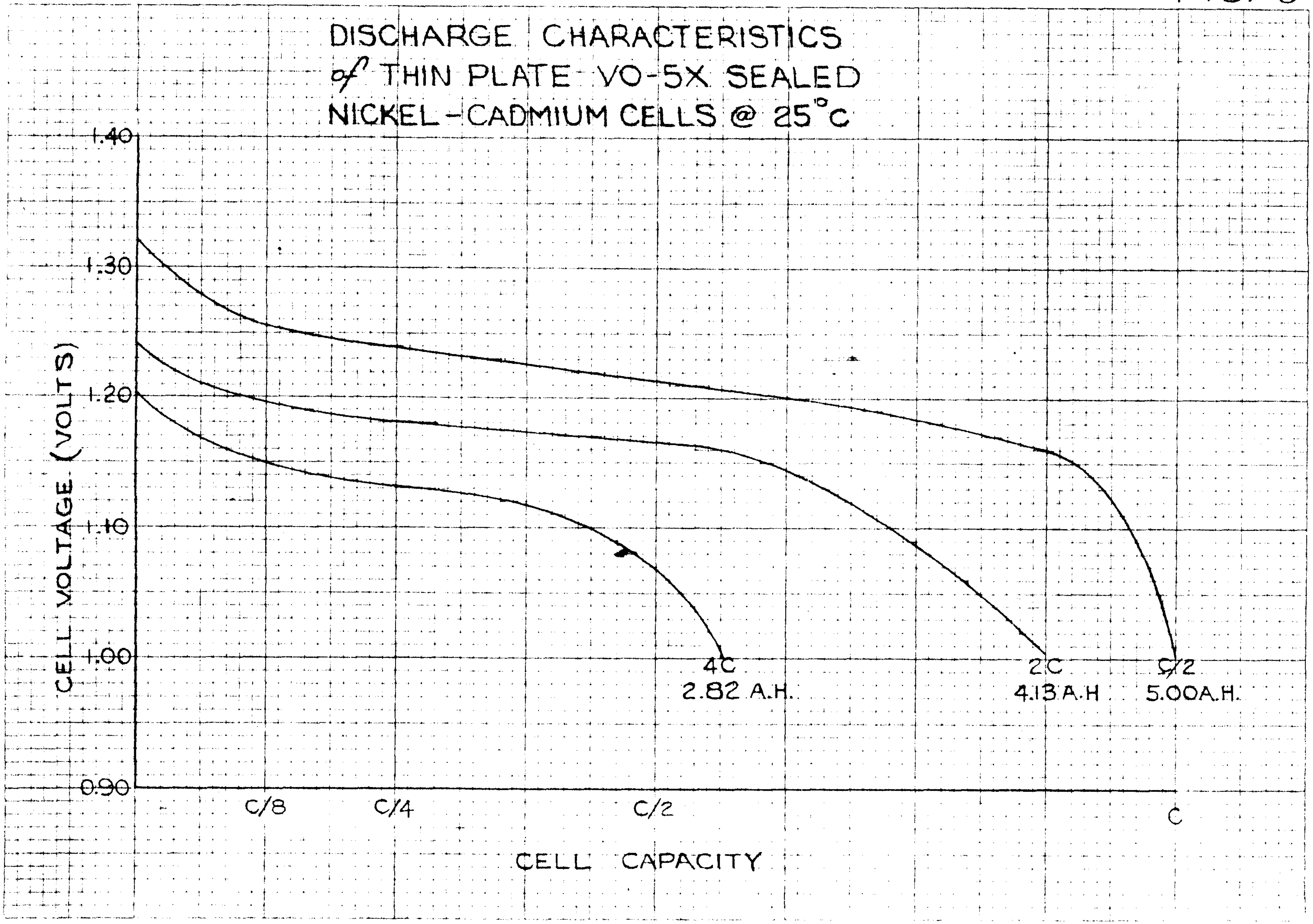


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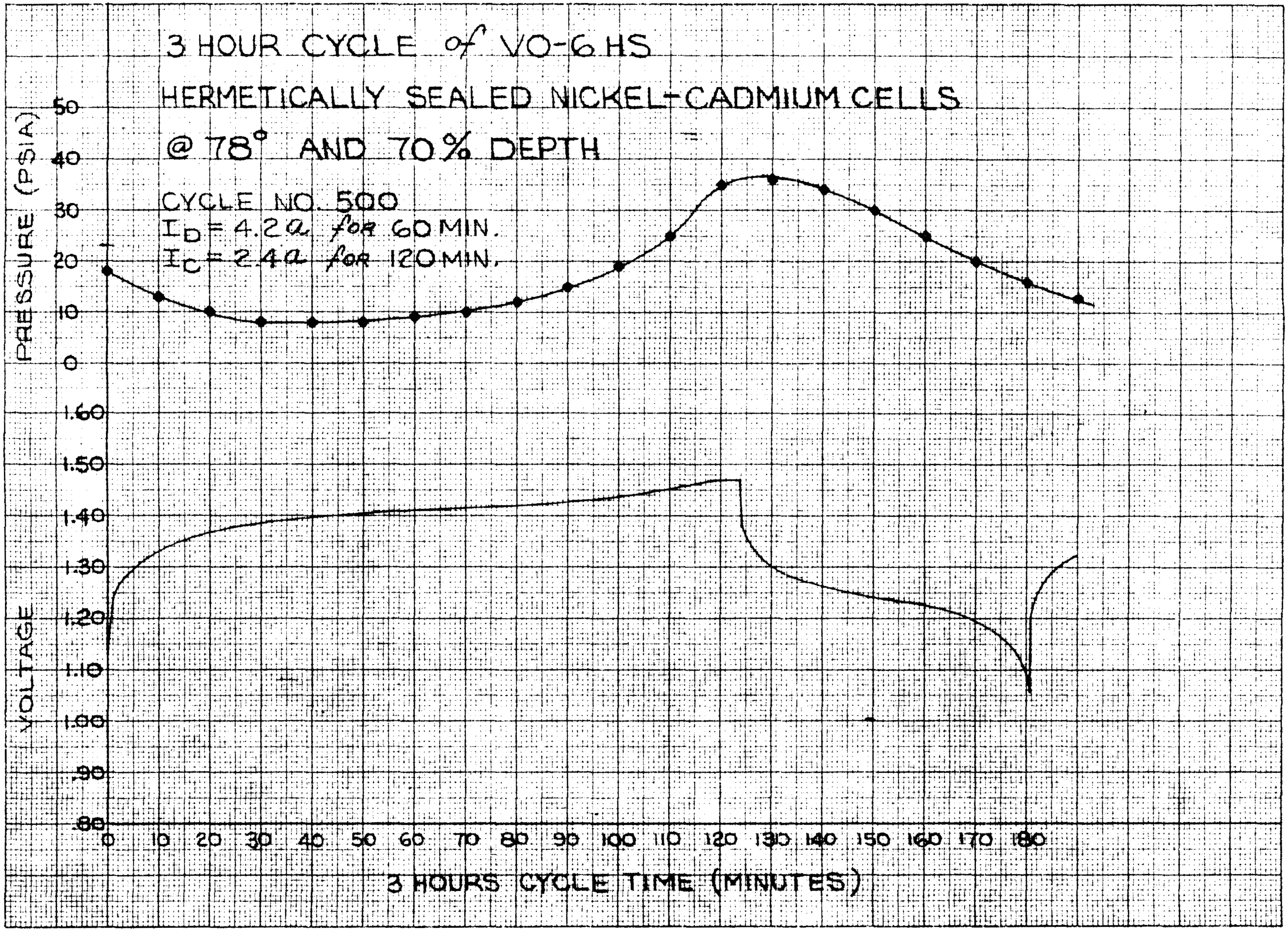
FIG. 10



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CAPACITY of VO-6 CELLS AFTER VARIOUS CHARGE ROUTINES

FIG. 11

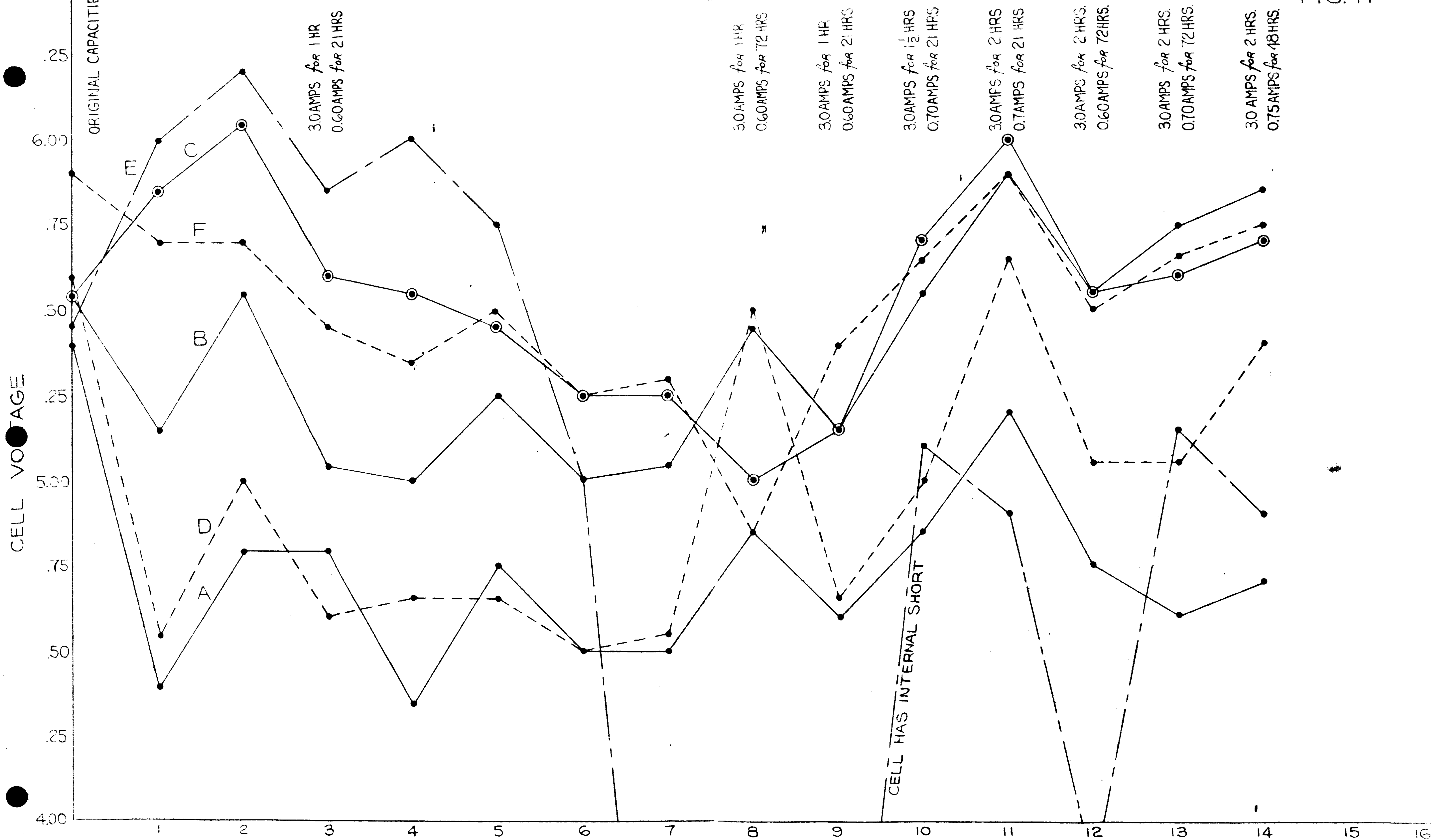

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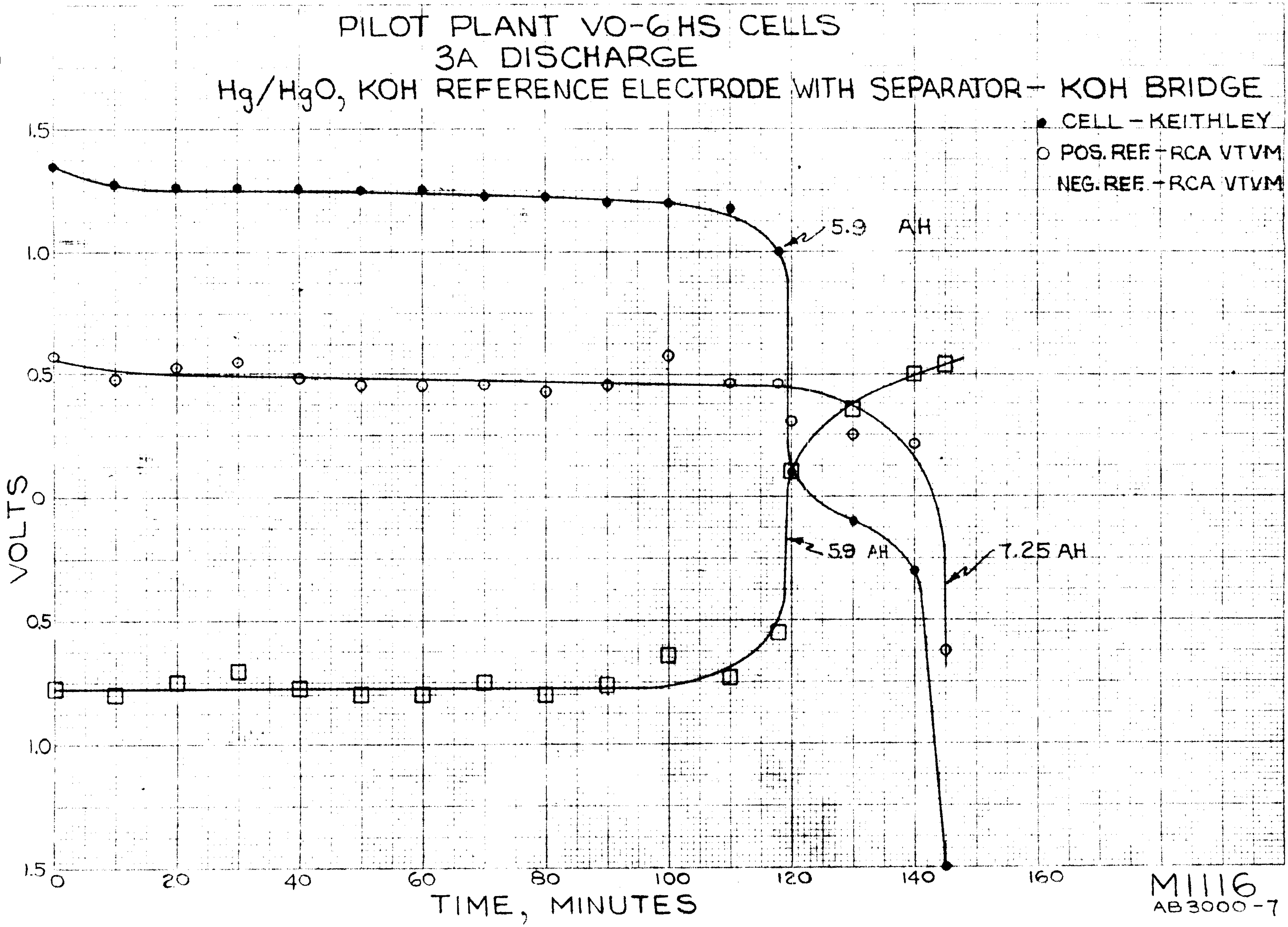
FIG. 12



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